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(54) Silver halide photographic emulsion

Photographische Silberhalogenidemulsion

Emulsion photographique à l'halogénure d'argent

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EP-A- 0 484 927

- **PATENT ABSTRACTS OF JAPAN vol. 12, no. 354 (P-761)(3201) 22 September 1988**

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Description

This invention relates to a silver halide photographic emulsion for use in silver halide photographic materials. More particularly, this invention relates to a silver halide photographic emulsion for use in silver halide photographic materials that are improved in sensitivity, graininess and keeping quality.

With the recent expansion of the use of imaging equipment such as cameras, the occasion to take pictures using silver halide photographic materials has also increased. This has led to the ever growing need to manufacture silver halide photographic materials that have higher sensitivity and that are capable of producing image of better quality.

One of the factors that govern the sensitivity and image quality of silver halide photographic materials is silver halide grains and efforts have heretofore been made in the photographic industry to develop silver halide grains that are suitable for the purpose of providing higher sensitivity and better image quality. However, if the size of silver halide grains is reduced as is often practiced in the art, the sensitivity tends to decrease; hence, there have been limits to the effort to satisfy both requirements for higher sensitivity and better image quality at the same time.

With a view to achieving even higher sensitivity and better image quality, various studies have been conducted to develop techniques that are capable of improving the sensitivity to size ratio per silver halide grain. Among the techniques proposed so far is the one of using tabular silver halide grains, as described in Unexamined Published Japanese Patent Application Nos. 111935/1983, 111936/1983, 111937/1983, 113927/1983, 99433/1984, etc. Compared to silver halide grains as crystals of "regular" shapes such as octahedra, tetradecahedra and hexahedra, tabular silver halide grains have a large surface area given the same grain volume and, hence, more sensitizing dyes can be adsorbed on the surfaces of tabular silver halide grains to provide even higher sensitivity.

Unexamined Published Japanese Patent Application No. 92942/1988 proposes the technique of providing a core of the higher silver iodide content in the interior of tabular silver halide grains; Unexamined Published Japanese Patent Application No. 151618/1988 proposes the technique of using hexagonal tabular silver halide grains; and Unexamined Published Japanese Patent Application No. 163451/1988 proposes the technique of using tabular silver halide grains of such a shape that the ratio of grain thickness to the longest distance between twinned faces is at least 5. These techniques are shown to be effective in improving sensitivity and graininess.

Further, Unexamined Published Japanese Patent Application No. 106746/1988 describes tabular silver halide grains having a layer structure that extends substantially parallel to two opposing principal planes, and Unexamined Published Japanese Patent Application No. 279237/1989 describes the technique of using tabular silver halide grains that have a layer structure that is bound by planes substantially parallel to two opposing principal planes and whose average silver iodide content of the outermost layer is at least 1 mol% higher than the average silver iodide content of the silver halide grains taken as a whole. Besides, Unexamined Published Japanese Patent Applciation No. 183644/1989 discloses the technique of using tabular silver halide grains that are completely uniform in the distribution of silver iodide in silver halide grains containing silver iodide.

However, all of the conventional techniques described above are limited in their ability to satisfy both requirements for higher sensitivity and better image quality and they are insufficient for the purpose of achieving the high levels of sensitivity and image quality that are required for modern versions of light-sensitive materials. Hence, it has been desired to develop more effective techniques.

The present invention has been accomplished under these circumstances and has, as an object, providing a silver halide photographic emulsion that yields silver halide photographic materials having high sensitivity, good graininess and satisfactory keeping quality.

The present invention provides a light-sensitive silver halide photographic emulsion comprising tabular silver halide grains, each of said tabular silver halide grains having an internal phase and an outermost layer that have different silver iodide contents.

According to the invention, said tabular silver halide grains have a total projected area of at least 50% of all the grains in said emulsion, the average silver iodide content of said tabular silver halide grains being at least 5 mol%, said internal phase having a silver iodide content of at least 18 mol %, said outermost layer having a silver iodide content of not more than 0.4 mol%, and a sectional plane cutting each of at least 50% in number of all the tabular silver halide grains in a direction that passes through the center of said tabular silver halide grain and being perpendicular to two parallel major faces satisfies the following relation:

$$90/100 \leq a/b \leq 100/90$$

where a is an average silver iodide content of a region defined by a distance over 9d/20 as measured from the centre of said tabular silver halide grain in a direction perpendicular to the major faces, where d is the distance between the two parallel major faces in association with the sectional plane, and b is an average silver iodide content of a region defined by a distance over 9l/20 as measured from the center of said tabular silver halide grain in a direction parallel

to the major faces, where l is the distance between two opposing surfaces of the grain as measured in a direction that passes through the centre of said tabular silver halide grain and which is parallel to the major faces in association with the sectional plane.

The term "tabular silver halide grains" as used herein means those grains which have two opposing parallel major faces. The aspect ratio, or the diameter to thickness ratio, of tabular silver halide grains to be used in the present invention is preferably from 1 to less than 5 on average, more preferably from 1.1 to less than 4.5, and most preferably from 1.2 to less than 4. The average value of the aspect ratio can be obtained by averaging the diameter to thickness ratios of all tabular silver halide grains present.

The diameter of a tabular silver halide grain is expressed in terms of the diameter of an equivalent circle of the projected area of that grain (i.e., the diameter of a circle having the same projected area as that grain); preferably, such diameter is 0.1 - 5.0 μm, more preferably 0.2 - 4.0 μm, and most preferably 0.3 - 3.0 μm.

The silver halide photographic emulsion of the present invention is such that when it is coated in a single layer with care being taken to insure that the silver halide grains contained in said emulsion will not overlap one another, at least 50%, preferably at least 60%, more preferably at least 70%, of the total projected area of all silver halide grains in the emulsion is assumed by tabular silver halide grains.

The tabular silver halide grains as used in the present invention are classified crystallographically as twins. A "twin" is a silver halide crystal having one or more twinned faces in one grain; morphological classification of twins is described in detail by E.Klein and E.Moisar in Photogr. Korresp., 99, 99 and ibid., 100, 57.

The tabular silver halide grains to be contained in the silver halide photographic emulsion of the present invention are preferably monodispersed. Grains are called "monodispersed" if their monodispersity as defined by the following formula is less than 20%.

(S.D. of diameter/av. diameter) × 100 = monodispersity (%). Preferably, the monodispersity of the tabular silver halide grains is less than 18%, more preferably less than 15%.

The tabular silver halide grains to be contained in the silver halide photographic emulsion of the present invention are preferably comprised of the major faces in the shape of hexagon assume at least 50%, more preferably at least 60%, most preferably at least 70%, in number of the tabular silver halide grains present.

A "tabular silver halide grain comprised of the major faces in the shape of hexagon" as used in the present invention has two parallel twinned faces. A tabular silver halide grain may be said "to be comprised of the major faces in the shape of hexagon" if the ratio of the longest side to the shortest side of the six sides of the grain, as viewed in a direction perpendicular to the parallel major faces, is preferably not greater than 2, more preferably not greater than 1.8, and most preferably not greater than 1.5.

The average diameter of the tabular silver halide grains to be used in the present invention can be measured on an electron micrograph of the silver halide emulsion of the present invention. With an electron micrograph enlarged by a magnification of 1×10^4 - 5×10^4, the projected areas of hexagonal and triangular silver halide grains are measured and the average diameter of equivalent circles is calculated.

The tabular silver halide grains contained in the silver halide photographic emulsion of the present invention have an average silver iodide content of at least 5 mol%, more preferably at least 5.5 mol%, and most preferably at least 6 mol%. Specifically, the average silver iodide content can be measured by an EPMA method which is well known in the art.

The tabular silver halide grains contained in the silver halide photographic emulsion of the present invention have a high silver iodide phase in the internal phase of each grain, with the AgI content of that phase being at least 18 mol%, preferably at least 20 mol%, and most preferably at least 25 mol%.

The silver iodide content of the internal phase of grains to be used in the present invention can be measured by a method of X-ray microanalysis according to the following procedure: silver halide grains to be examined are dispersed in an observation grid which has an energy-dispersive X-ray analyzer mounted on an electron microscope; under cooling with liquid nitrogen, the magnification is set in such a way that one grain is located within the view field of CRT; the intensities of AgLα and ILα rays are integrated for a predetermined time; the silver iodide content of a particular grain can be computed on the basis of the ILα/AgLα intensity ratio using a preliminarily constructed calibration curve.

The tabular silver halide grains to be contained in the silver halide photographic emulsion of the present invention have an average silver iodide content of no higher than 0.4 mol%, preferably no higher than 0.3 mol%, more preferably no higher than 0.2 mol%, in the outermost layer. Specifically, the average silver iodide content in the outermost layer of the tabular silver halide grains to be contained in the silver halide photographic emulsion of the present invention can be measured by X-ray photoelectron spectroscopy (XPS).

The tabular silver halide grains contained in the silver halide photographic emulsion of the present invention are such that a sectional plane cutting each of said silver halide grains in a direction that passes through its center and which is perpendicular to two parallel major faces satisfies the relation:

$90/100 \leq a/b \leq 100/90$, preferably $92/100 \leq a/b \leq 100/92$, more preferably $95/100 \leq a/b \leq 100/95$, where $\underline{a}$ is the average silver iodide content of regions that are defined by a distance of at least 9d/20 as measured from the center of said

silver halide grains in a direction that is perpendicular to the two parallel major faces (where d is the distance between the two parallel major faces in association with the sectional plane), and b is the average silver iodide content of regions that are defined by a distance of at least 9ℓ/20 as measured from the center of said silver halide grains in a direction that is parallel to the two parallel major faces (where ℓ is the distance between two opposing surfaces of a grain as measured in a direction that passes through the center of said silver halide grains and which is parallel to the two parallel major faces in association with the sectional plane).

In the tabular silver halide grains contained in the silver halide photographic emulsion of the present invention, the proportion of tabular silver halide grains that satisfy the relation $90/100 \leq a/b \leq 100/90$ is at least 50%, more preferably at least 60%, and most preferably at least 70%, in number of all the tabular silver halide grains contained in the silver halide photographic emulsion of interest.

As regards the tabular silver halide grains contained in the silver halide photographic emulsion of the present invention, d, or the distance between the two parallel major faces in association with a sectional plane through each grain, and ℓ, or the distance between two opposing surfaces of a grain as measured in a direction that passes through the center of said silver halide grains and which is parallel to the two parallel major faces in association with the sectional plane, can be determined by the following process: the gelatin of the silver halide photographic emulsion of the present invention is decomposed with a protease; thereafter, the tabular silver halide grains in said emulsion are embedded in a methacrylic resin, which is then cut with a diamond cutter to prepare a specimen 800 Å thick; the specimen is examined under a transmission electron microscope and a picture in the field of view is taken; the distances d and ℓ are measured on the picture.

As regards the tabular silver halide grains contained in the silver halide photographic emulsion of the present invention, a, or the average silver iodide content of regions that are defined by a distance of at least 9d/20 as measured from the center of said silver halide grains in a direction that is perpendicular to the two parallel major faces and b, or the average silver iodide content of regions that are defined by a distance of at least 9 /20 as measured from the center of said silver halide grains in a direction that is parallel to the two parallel major faces, can each be determined on the same specimen as used in the aforementioned examination under a transmission electron microscopy by averaging the silver iodide contents as measured at two sites of a grain that are positioned in point symmetry with respect to the center of that grain by means of point analysis using the EPMA method which is well known in the art.

The silver halide photographic emulsion of the present invention can generally be produced by a process in which a silver halide emulsion that is prepared by the method described in Japanese Patent Application No. 408178/1990 is used as a seed from which growth is effected at a pH of no higher than 7.5 using an aqueous solution of ammoniacal silver nitrate, which process is characterized in that growth until the end of the formation of a high silver iodide phase is effected in a pAg region of no more than 8.5 and growth subsequent to the formation of that high silver iodide phase is effected in a pAg region of at least 9.2.

For other conditions to be adopted to produce the silver halide photographic emulsion of the present invention, namely, conditions other than the use of the silver halide seed emulsion prepared by the method described in Japanese Patent Application No. 408178/1990, growth in an aqueous solution of ammoniacal silver nitrate at a pH of 7.5, and the pAg regions for growth before and after the formation of the high silver iodide phase in the interior of grains, optimam conditions can be selected with reference being made to known methods as described in Unexamined Published Japanese Patent Application Nos. 6643/1986, 14630/1986, 112142/1986, 157024/1987, 18556/1987, 92942/1988, 151618/1988, 163451/1988, 220238/1988 and 311244/1988.

It is also possible to perform flocculation or noodle washing in the usual manner.

The silver halide grains to be used in the present invention are composed of silver iodobromide or silver iodochlorobromide. They may be of a surface latent image type or an internal latent image type.

The silver halide photographic emulsion of the present invention can preferably be used in silver halide color photographic materials.

When composing a color photographic material using the silver halide photographic emulsion of the present invention, the latter should already be subjected to physical ripening, chemical ripening and spectral sensitization. Additives that can be used in those steps are described in Research Disclosure Nos. 17643, 18716 and 308119 (which are respectively referred to as RD 17643, RD 18716 and RD 308119). Relevant portions are cited below from the respective RDs.

Additive	(RD 308119)	(RD 17643)	(RD 18716)
Chemical sensitizer	996 III-A	23	648
Spectral sensitizer	996 IV-A-A,B,C, D,H,I,J	23-24	648-649
Supersensitizer	996 IV-A-E,J	23-24	648-649
Antifoggant	998 VI	24-25	649

(continued)

Additive	(RD 308119)	(RD 17643)	(RD 18716)
Stabilizer	998 VI	24-25	649

Known photographic addenda that can be used in composing a color photographic material using the silver halide photographic emulsion of the present invention are also described in the three issues of Research Disclosure. Relevant portions are cited below from the respective RDs.

Additive	(RD 308119)	(RD 17643)	(RD 18716)
Anti-color contamination agent	1002 VII-I	25	650
Dye image stabilizer	1001 VI-J	25	
Optical brightening agent	998 V	24	
UV absorber	1003 VIII-C, XIII C	25-26	
Light absorber	1003 VIII	25-26	
Light scattering agent	1003 VIII		
Filter dye	1003 VIII	25-26	
Binder	1003 IX	26	651
Antistatic agent	1006 XIII	27	650
Hardener	1004 X	26	651
Plasticizer	1006 XII	27	650
Lubricant	1006 XII	27	650
Activator/ coating aid	1005 XI	26-27	650
Matting Agent	1007 XVI		
Developing agent (contained in photographic material)	1011 XXB		

Various couplers can be used when composing a color photographic material using the silver halide photographic emulsion of the present invention and specific examples of the couplers that can be used are described in two of the three issues of Research Disclosure. Relevant portions are cited below from the respective RDs.

Coupler	(RD 308119)		(RD 17643)
Yellow coupler	1001	VII-D	VII C-G
Magenta coupler	1001	VII-D	VII C-G
Cyan coupler	1001	VII-D	VII C-G
Colored coupler	1002	VII-G	VII G
DIR coupler	1001	VII-F	VII F
BAR coupler	1002	VII-F	
Other useful residue releasing couplers	1001	VII-F	
Alkali-soluble coupler	1001	VII-E	

The additives to be used when composing a color photogaphic material using the silver halide photographic emulsion of the present invention can be incorporated by various methods such as the method of dispersion described in RD 308119 under XIV.

When composing a color photographic material using the silver halide photographic emulsion of the present invention, various bases can be used as described in RD I7643 on page 28, RD 18716 on pages 647 - 648 and RD 308119 under XVII.

A color photographic material using the silver halide photographic emulsion of the present invention may be provided with a filter layer, an intermediate layer and other auxiliary layers as described in RD 308119 under VII-K.

A color photographic material using the silver halide photographic emulsion of the present invention may adopt various layer arrangements including a conventional layer order, an inverse layer order and a unit structure, as described in RD 308119 under VII-K.

The silver halide photographic emulsion of the present invention can preferably be applied to various color photographic materials as typified by color negative films for general use or for motion pictures, color reversal films for slides or TV, color papers, color positive films and color reversal papers.

The color photographic material using the silver halide photographic emulsion of the present invention can be processed by conventional methods as described in RD I7643 on pages 28 - 29, RD 18716 on page 615, and RD 308119 under XIX.

The following examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting.

Example 1

(1) Preparation of comparative emulsion (Em-1)

A comparative emulsion containing core/shell structured) octahedral silver iodobromide grains (average grain size: 1.1 μm; AgI content: 8 mol%) was prepared by the method described in Unexamined Published Japanese Patent Applciation No. 138538/1985.

Other comparative emulsions Em-2, Em-3 and Em-4 each containing core/shell structured tabular silver halide grains were prepared by the following methods.

(2) Preparation of comparative emulsion (Em-2)

To 5 L of a 3.0% aqueous gelatin solution containing 44.9 g of potassium bromide, 119 ml of an aqueous solution containing 9.76 g of potassium bromide and 119 ml of an aqueous solution containing 13.96 g of silver nitrate were

added at equal flow rates under agitaion at 70°C and at pH of 5.8 by a double-jet method with pAg being controlled at 9.6. In the next step, 2.896 L of an aqueous solution containing 492 g of silver nitrate and 2.896 L of an aqueous solution containing 230 g of potassium bromide and 159 g of potassium iodide were added at equal flow rates by a double-jet method with pAg being controlled at 7.5. Then, 4.3 L of an aqueous solution containing 1534 g of silver nitrate and 4.3 L of an aqueous solution containing 1075 g of potassium bromide were added at equal flow rates by a double-jet method with pAg being controlled at 8.4. Subsequently, the mixture was desalted at 40°C and gelatin was added to effect re-dispersion.

(3) Preparation of comparative emulsion (Em-3)

To 4 L of a 2.5% aqueous gelatin solution containing 35.9 g of potassium bromide, 119 ml of an aqueous solution containing 9.76 g of potassium bromide and 119 ml of an aqueous solution containing 13.96 g of silver nitrate were added at equal flow rates under agitation at 70°C and at pH 5.8 by a double-jet method with pAg being controlled at 9.6. In the next step, 2.254 L of an aqueous solution containing 536 g of silver nitrate and 2.254 L of an aqueous solution containing 290 g of potassium bromide and 120 g of potassium iodide were added at equal flow rates by a double-jet method with pAg being controlled at 8.9. Then, 5.847 L of an aqueous solution containing 1490 g of silver nitrate and 5.847 L of an aqueous solution containing 1044 g of potassium bromide were added at equal flow rates by a double-jet method with pAg being controlled at 9.2, whereupon tabular silver halide grains were precipitated.

After the end of addition of all components, desalting was effected at 40°C and gelatin was added to effect re-dispersion.

(4) Preparation of comparative emulsion (Em-4)

To 5 L of a 3.5% aqueous gelatin solution containing 44.9 g of potassium bromide, 119 ml of an aqueous solution containing 9.76 g of potassium bromide and 119 ml of an aqueous solution containing 13.96 g of silver nitrate were added at equal flow rates under agitation at 70°C and at pH 5.8 by a double-jet method with pAg being controlled at 9.6. In the next step, 1.753 L of an aqueous solution containing 536 g of silver nitrate and 1.753 L of an aqueous solution containing 290 g of potassium bromide and 120 g of potassium iodide were added at equal flow rates by a double-jet method with pAg being controlled at 8.0. Then, 3.508 L of an aqueous solution containing 1490 g of silver nitrate and 3.508 L of an aqueous solution containing 1044 g of potassium bromide were added at equal flow rates by a double-jet method with pAg being controlled at 8.6, whereupon tabular silver halide grains were precipitated.

After the end of addition of all components, desalting was effected at 40°C and gelatin was added to effect re-dispersion.

(5) Preparation of monodispersed spherical seed emulsion (T-1)

A monodispersed spherical seed emulsion (T-1) was prepared by the following method with reference being made to the disclosure in Japanese Patent Application No. 408178/1990.

Solution A	Ossein gelatin	80.0 g
	Potassium bromide	39.0 g
	Potassium iodide	11.7 g
	Water	to make 8 L
Solution B	Silver nitrate	1.2 kg
	Water	to make 1.6 L
Solution C	Ossein gelatin	32.2 g
	Potassium bromide	840 g
	Water	to make 1.6 L
Solution D	Aqueous ammonia (28%)	470 ml

With solution A being stirred vigorously at 40°C, solutions B and C were added by a double-jet method over 11 min to form nuclei. During the nucleation stage, the pBr of the mixture was held at 1.09 - 1.70. Thereafter, the temperature of the mixture was lowered to 30°C over 12 min, followed by ripening for 18 min. Then, solution D was added over 1 min, followed by ripening for 5 min. During the ripening stage, the KBr concentration was held at 0.07 mol/L and the ammonia concentration was held at 0.63 mol/L. After pH adjustment to 6.0, the mixture was immediately desalted and washed with water. Examination of the particles in the seed emulsion under an electron microscope

showed that it was a monodispersed spherical emulsion having an average grain size of 0.30 μm with the spread of distribution being 18%.

Using the seed emulsion (T-1), silver halide emulsions of the present invention Em-5, Em-6, Em-7, and Em-8, were prepared in the following manner.

(6) Preparation of silver halide emulsion (Em-5) of the present invention

Using the seed emulsion (T-1) and the five solutions described below, a silver halide emulsion of the present invention, Em-5, was prepared.

G-10

Ossein gelatin (av. mol. wt. 10^5)	262.5 g
Compound-I	1.5 ml
Ammonia (28% aq. sol.)	528.0 ml
Acetic acid (56% aq. sol.)	795.0 ml
Methanol solution containing 0.001 mole of I_2	50.0 ml
Water	to make 4450.0 ml

Compound-I: Aqueous solution in ethanol of 10% sodium salt of polyisopropylene-polyethyleneoxy-disuccinic acid ester

H-10

Aqueous solution of 3.5 N potassium bromide containing 4.0 wt% ossein gelatin

S-10

Aqueous solution of 3.5 N ammoniacal silver nitrate

MC-10

Fine grained emulsion composed of 3 wt% ossein gelatin and silver iodide grains (average particle size, 0.04 μm)

MC-10 was prepared by the following method: 2,000 ml each of aqueous solutions containing 7.06 moles of silver nitrate and 7.06 moles of potassium iodide were added over 10 min to 5,000 ml of a 6.0 wt% gelatin solution containing 0.06 mole of potassium iodide; during the formation of fine grains, the pH was adjusted to 2.0 with nitric acid and the temprerature of the mixture was held at 30°C. After the formation of grains, the mixture was adjusted to a pH of 6.0 with an aqueous solution of sodium carbonate.

MC-20

Fine grained emulsion that was composed of 3 wt% ossein gelatin and silver bromide grains (average particle size, 0.04 μm) and which was prepared by the same method as that for preparing MC-10.

Seed emulsion (T-1) in an amount equivalent to 0.286 mole was added to the solution G-10 in the reaction vessel as it was stirred well with the temperature, pAg and pH being held at 70°C, 8.3 and 7.2, respectively.

Thereafter, H-10, S-10 and MC-10 were charged into the reaction vessel at an accelerated speed by a triple-jet method over 140 min at the flow rates necessary to produce the silver halide composition shown in Talbe 1, whereby silver halide grains were grown until the silver addition reached 78%.

Subsequently, MC-20 was added over 10 min, followed by ripening for 11 min so that silver halide grains would grow until the silver addition reached 100%.

During the grain growth, the pH and pAg were controlled to the values shown in Table 1 by feeding an aqueous solution of potassium bromide and an aqueous solution of acetic acid into the reaction vessel.

After the formation of grains, they were washed with water in accordance with the disclosure in Japanese Patent Application No. 4003/1990 and, thereafter, gelatin was added to effect re-dispersion.

Table 1

Silver addition (%)	0.0	9.0	13.0	26.0	33.0	36.0	46.0	78.0	100.0
AgI content of the time of addition (mol%)	10	→ 10	→ 25	→ 25	→ 10	→ 10	→ 8 ↓ 0	→	0
pH	7.2	→	7.2 ↓ 6.5	→	→	→	→	→	6.5
pAg	8.3	→	8.3 ↓ 9.7	→	→	→	→	→	9.7

Note: ↓ denotes a stepwise change and → denotes a continuous change.

(7) Preparation of silver halide emulsion (Em-6) of the present invention

A silver halide emulsion of the present invention, Em-6, was prepared using the seed emulsion (T-1) and the five solutions, G-10, H-10, S-10, MC-10 and MC-20, which were used in preparing Em-5.

Seed emulsion (T-1) in an amount equivalent to 0.286 mole was added to the solution G-10 in the reaction vessel as it was stirred well with the temperature, pAg and pH being held at 70°C, 8.0 and 7.0, respectively.

Thereafter, H-10, S-10 and MC-10 were charged into the reaction vessel at an accelerated speed by a triple-jet method over 170 min at the flow rates necessary to produce the silver halide composition shown in Table 2, whereby silver halide grains were grown until the silver addition reached 78%.

Subsequently, MC-20 was added over 10 min, followed by ripening for 10 min so that silver halide grains would grow until the silver addition reached 100%.

During the grain growth, the pH and pAg were controlled to the values shown in Table 2 by feeding an aqueous solution of potassium bromide and an aqueous solution of acetic acid into the reaction vessel.

After the formation of grains, they were washed with water in accordance with the disclosure in Japanese Patent Application No. 4003/1990 and, thereafter, gelatin was added to effect re-dispersion.

Table 2

Silver addition (%)	0.0	9.0	13.0	26.0	33.0	36.0	46.0	78.0	100.0
AgI content of the time of addition (mol%)	10	→ 10	→ 30	→ 30	→ 10	→ 10	→ 8 ↓ 0	→	0
pH	7.0	→	7.0 ↓ 6.5	→	→	→	→	→	6.5
pAg	8.0	→	8.0 ↓ 9.4	→	→	→	9.4 →	9.7 →	9.7

Note: ↓ denotes a stepwise change and → denotes a continuous change.

(8) Preparation of silver halide emulsion (Em-7) of the present invention

A silver halide emulsion of the present invention, Em-7, was prepared using the seed emulsion (T-1) and the five solutions, G-10, H-10, S-10, MC-10 and MC-20, which were used in preparing Em-5.

Seed emulsion (T-1) in an amount equivalent to 0.286 mole was added to the solution G-10 in the reaction vessel as it was stirred well with the temperature, pAg and pH being held at 70°C, 8.1 and 7.2, respectively.

Thereafter, H-10, S-10 and MC-10 were charged into the reation vessel at an accelerated speed by a triple-jet method over 150 min at the flow rates necessary to produce the silver halide composition shown in Talbe 3, whereby silver halide grains were grown until the silver addition reached 78%.

Subsequently, MC-20 was added over 10 min, followed by ripening for 10 min so that silver halide grains would grow until the silver addition reached 100%.

During the grain growth, the pH and pAg were controlled to the values shown in Table 3 by feeding an aqueous solution of potassium bromide and an aqueous solution of acetic acid into the reaction vessel.

After the formation of grains, they were washed with water in accordance with the disclosure in Japanese Patent Application No. 4003/1990 and, thereafter, gelatin was added to effect re-disperesion.

Table 3

Silver addition (%)	0.0	9.0	13.0	26.0	33.0	36.0	46.0	78.0	100.0
AgI content of the time of addition (mol%)	10	10	30	30	10	10	8 ↓ 0	→	0
pH	7.2	→	7.2 ↓	6.5	→				6.5
pAg	8.2	→	8.2 ↓	9.5	→		9.5 →	9.7 →	9.7

Note: ↓ denotes a stepwise change and → denotes a continuous change.

(9) Preparation of silver halide emulsion (Em-8) of the present invention

A silver halide emulsion of the present invention, Em-8, was prepared using the seed emulsion (T-1) and the five solutions, G-10, H-10, S-10, MC-10 and MC-20, which were used in preparing Em-5.

Seed emulsion (T-1) in an amount equivalent to 0.286 mole was added to the solution G-10 in the reaction vessel as it was stirred well with the temperature, pAg and pH being held at 70°C, 8.4 and 7.0, respectively.

Thereafter, H-10, S-10 and MC-10 were charged into the reaction vessel at an accelerated speed by a triple-jet method over 125 min at the flow rates necessary to produce the silver halide composition shown in Table 4, whereby silver halide grains were grown until the silver addition reached 78%.

Subsequently, MC-20 was added over 10 min, followed by ripening for 10 min so that silver halide grains would grow until the silver addition reached 100%.

During the grain growth, the pH and pAg were controlled to the values shown in Table 4 by feeding an aqueous solution of potassium bromide and an aqueous solution of acetic acid into the reaction vessel.

After the formation of grains, they were washed with water in accordance with the disclosure in Japanese Patent Application No. 4003/1990 and, thereafter, gelatin was added to effect re-dispersion.

Table 4

Silver addition (%)	0.0	9.0	13.0	26.0	33.0	36.0	46.0	78.0	100.0
AgI content of the time of addition (mol%)	10	10	22	22	10	10	8 ↓ 0	→	0
pH	7.0	→	7.0 ↓	6.5	→	→	→	→	6.5
pAg	8.4	→	8.4 ↓	10.1	→	→	→	→	10.1

Note: ↓ denotes a stepwise change and → denotes a continuous change.

The thus prepared silver halide emulsions Em-1 to Em-8 were examined under an electron microscope to investigate various parameters. In addition, the average AgI content of each emulsion was measured by EPMA; the AgI content of the interior of silver halide grains was measured by X-ray microanalysis; the average AgI content of silver halide grains in the outermost layer was measured by XPS. Furthermore, point analysis was conducted by EPMA to determine a/b for each emulsion. The results of the microscopic examination and the various measurements are shown in Table 5.

Table 5

	Emulsion No.	Shape of silver halide grain	Percentage of the total projected area occupied by tabular grains	Average aspect ratio of tabular grains	Diameter of equivalent circle of the projected area of silver halide grains (μm)	Percentage of the number of tabular grains occupied by grains comprised of the major faces in the shape of hexagon	Monodispersity (%)	Average AgI content of silver halide grains (mol%)	AgI content of the high AgI phase in the interior of grains (mol%)	Average AgI content of silver halide grains in the outermost layer (mol%)	a/b
Comparison	Em-1	octahedral	-	-	1.1	-	15	8	20	1.2	1.6
	Em-2	tabular	60	4.0	1.5	62	22	8	33	0.6	1.3
	Em-3	tabular	75	6.0	1.7	55	28	6	23	1.0	1.7
	Em-4	tabular	65	4.0	1.4	70	20	6	23	1.6	1.9
Invention	Em-5	tabular	75	3.0	1.37	60	20	7.3	25	0.4	1.09
	Em-6	tabular	80	2.0	1.2	72	15	8.2	30	0.1	0.98
	Em-7	tabular	70	2.5	1.3	80	12	8.2	30	0.2	1.03
	Em-8	tabular	70	3.5	1.45	66	18	6.7	22	0.4	1.06

Silver halide emulsions Em-1 to Em-8 were subjected to optimal chemical sensitization. The sensitized emulsions were used in accordance with the formula indicated below, in which each emulsion is designated as Emulsion-A. Layers having the compositions described below were formed successively on triacetyl cellulose film bases, with the first layer being positioned the closest to the base, thereby preparing eight samples (Nos. 11 - 18) of multilayered color photographic material.

Unless otherwise noted, the amounts of addition of various ingredients are expressed in grams per square meter. The amounts of silver halides and colloidal silver are expressed in terms of silver, and the amounts of sensitizing dyes are expressed in moles per mole of silver.

First layer: Anti-halo layer

Black colloidal silver	0.16
UV absorber (UV - 1)	0.20
High-boiling organic solvent (Oil - 1)	0.16
Gelatin	1.23

Second layer: Intermediate layer

Compound (SC - 1)	0.15
High-boiling organic solvent (Oil - 2)	0.17
Gelatin	1.27

Third layer: Less red-sensitive layer

AgIBr emulsion (av. grain size = 0.38 μm; AgI = 8.0 mol%)	0.50

AgIBr emulsion (av. grain size = 0.27 μm; AgI = 2.0 mol%)	0.21
Sensitizing dye (SD - 1)	2.8×10^{-4}
Sensitizing dye (SD - 2)	1.9×10^{-4}
Sensitizing dye (SD - 3)	1.9×10^{-5}
Sensitizing dye (SD - 4)	1.0×10^{-4}
Cyan coupler (C - 1)	0.48
Cyan coupler (C - 2)	0.14
Colored cyan coupler (CC - 1)	0.021
DIR compound (D - 1)	0.020
High-boiling solvent (Oil - 1)	0.53
Gelatin	1.30

Fourth layer: Moderately red-sensitive layer

AgIBr emulsion (av. grain size = 0.52 μm; AgI = 8.0 mol%)	0.62
AgIBr emulsion (av. grain size = 0.38 μm; AgI = 8.0 mol%)	0.27
Sensitizing dye (SD - 1)	2.3×10^{-4}
Sensitizing dye (SD - 2)	1.2×10^{-4}
Sensitizing dye (SD - 3)	1.6×10^{-5}
Sensitizing dye (SD - 4)	1.2×10^{-4}
Cyan coupler (C - 1)	0.15
Cyan coupler (C - 2)	0.18
Colored cyan coupler (CC - 1)	0.030
DIR compound (D - 1)	0.013

High-boiling solvent (Oil - 1)	0.30
Gelatin	0.93

Fifth layer: Highly red-sensitive layer

AgIBr emulsion (Emulsion A)	1.27
Sensitizing dye (SD - 1)	1.3×10^{-4}
Sensitizing dye (SD - 2)	1.3×10^{-4}
Sensitizing dye (SD - 3)	1.6×10^{-5}
Cyan coupler (C - 2)	0.12
Colored cyan coupler (CC - 1)	0.013
High-boiling solvent (Oil - 1)	0.14
Gelatin	0.91

Sixth layer: Intermediate layer

Compound (SC - 1)	0.09
High-boiling organic solvent (Oil - 2)	0.11
Gelatin	0.80

Seventh layer: Less green-sensitive layer

AgIBr emulsion (av. grain size = 0.38 μm; AgI = 8.0 mol%)	0.61
AgIBr emulsion (av. grain size = 0.27 μm; AgI = 2.0 mol%)	0.20
Sensitizing dye (SD - 4)	7.4×10^{-5}
Sensitizing dye (SD - 5)	6.6×10^{-4}
Magenta coupler (M - 1)	0.18
Magenta coupler (M - 2)	0.44
Colored magenta coupler (CM - 1)	0.12
High-boiling solvent (Oil - 2)	0.75
Gelatin	1.95

Eighth layer: Moderately green-sensitive layer

AgIBr emulsion (av. grain size = 0.59 μm; AgI = 8.0 mol%)	0.87
Sensitizing dye (SD - 6)	2.4×10^{-4}
Sensitizing dye (SD - 7)	2.4×10^{-4}
Magenta coupler (M - 1)	0.058
Magenta coupler (M - 2)	0.13
Colored magenta coupler (CM - 1)	0.070
DIR compound (D - 2)	0.025
DIR compound (D - 3)	0.002
High-boiling solvent (Oil - 2)	0.50
Gelatin	1.00

Ninth layer: Highly green-sensitive layer

AgIBr emulsion (Emulsion A)	1.27
Sensitizing dye (SD - 6)	1.4×10^{-4}
Sensitizing dye (SD - 7)	1.4×10^{-4}
Magenta coupler (M - 2)	0.084
Magenta coupler (M - 3)	0.064
Colored magenta coupler (CM - 1)	0.012
High-boiling solvent (Oil - 1)	0.27
High-boiling solvent (Oil - 2)	0.012
Gelatin	1.00

Tenth layer: Yellow filter layer

Yellow colloidal silver	0.08
Stain control agent (SC - 2)	0.15
Formaldehyde scavenger (HS - 1)	0.20
High-boiling solvent (Oil - 2)	0.19
Gelatin	1.10

Eleventh layer: Intermediate layer

Formaldehyde scavenger (HS - 1)	0.20
Gelatin	0.60

Twelfth layer: Less blue-sensitive layer

AgIBr emulsion (av. grain size = 0.38 μm; AgI = 8.0 mol%)	0.22
AgIBr emulsion (av. grain size = 0.27 μm; AgI = 2.0 mol%)	0.03
Sensitizing dye (SD - 8)	4.9×10^{-4}
Yellow coupler (Y - 1)	0.75
DIR compound (D - 1)	0.010
High-boiling solvent (Oil - 2)	0.30
Gelatin	1.20

Thirteenth layer: Moderately blue-sensitive layer

AgIBr emulsion (av. grain size = 0.59 μm; AgI = 8.0 mol%)	0.30
Sensitizing dye (SD - 8)	1.6×10^{-4}
Sensitizing dye (SD - 9)	7.2×10^{-5}
Yellow coupler (Y - 1)	0.10
DIR compound (D - 1)	0.010
High-boiling solvent (Oil - 2)	0.046
Gelatin	0.47

Fourteenth layer: Highly blue-sensitive layer

AgIBr emulsion (Emulsion A)	0.85
Sensitizing dye (SD - 8)	7.3×10^{-5}
Sensitizing dye (SD - 9)	2.8×10^{-5}
Yellow coupler (Y - 1)	0.11
High-boiling solvent (Oil - 2)	0.046
Gelatin	0.80

Fifteenth layer: First protective layer

AgIBr emulsion (av. grain size = 0.08 μm; AgI = 1.0 mol%)	0.40
UV absorber (UV - 1)	0.065
UV absorber (UV - 2)	0.10
High-boiling solvent (Oil - 1)	0.07
High-boiling solvent (Oil - 3)	0.07
Formaldehyde scavenger (HS - 1)	0.40
Gelatin	1.31

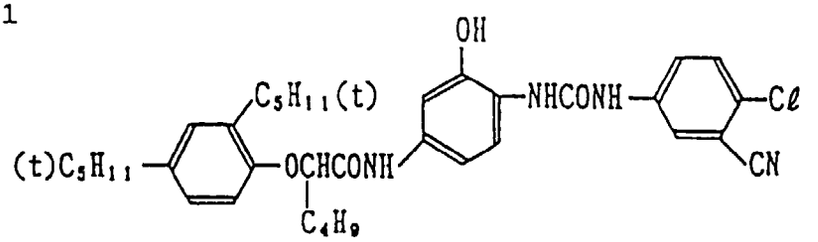
Sixteenth layer: Second protective layer

Alkali-soluble matting agent (av. grain size = 2 μm)	0.15
Polymethyl methacrylate (av. grain size = 3 μm)	0.04
Slip agent (WAX - 1)	0.04
Gelatin	0.55

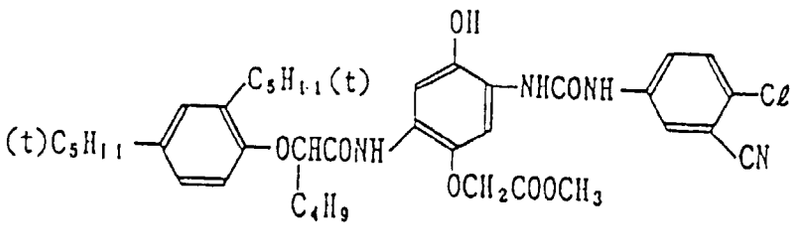
Besides the components listed above, the following reagents were also added: coating aid Su-1, dispersion aid Su-2, viscosity modifier, hardeners H-1 and H-2, stabilizer ST-1, anti-foggant AF-1, two kinds of AF-2 having weight average molecular weights of 10,000 and 1,100,000, and antiseptic DI-1. The last-mentioned DI-1 was added in an amount of 9.4 mg/m^2.

The structures of the compounds used in samples 1 - 8 are shown below.

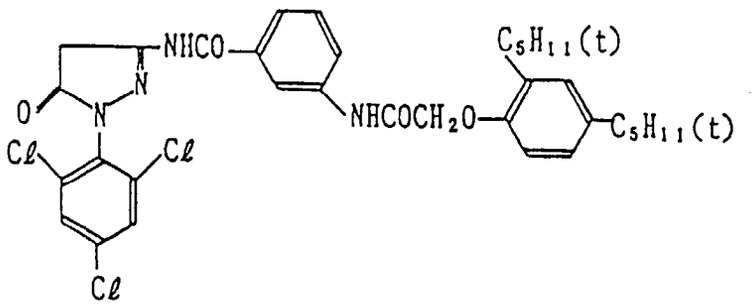
C - 1



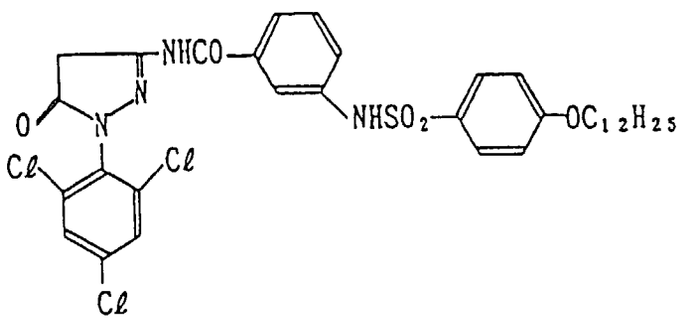
C - 2



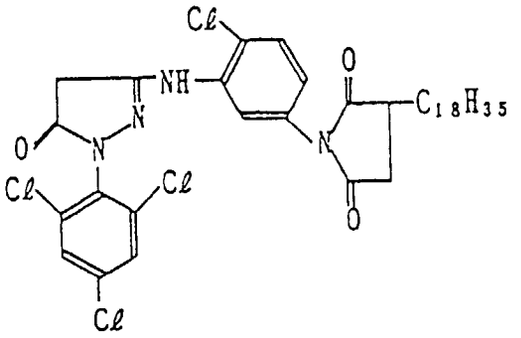
M - 1



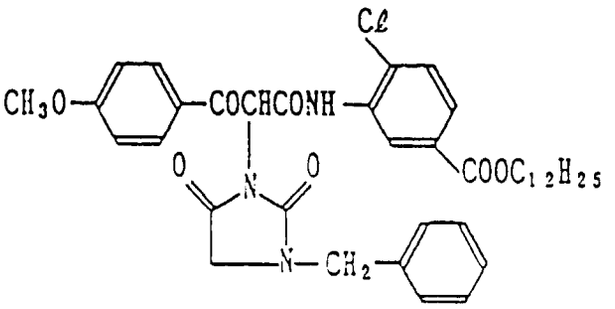
M - 2



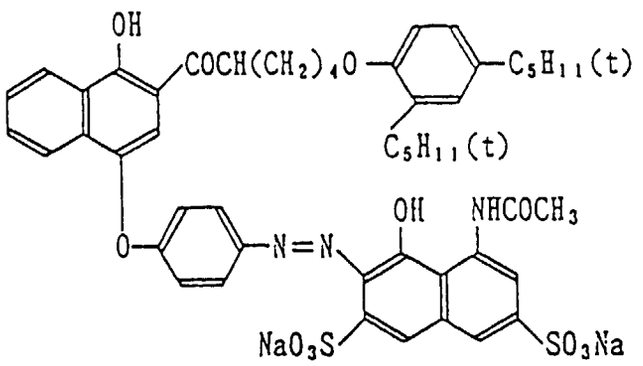
M - 3



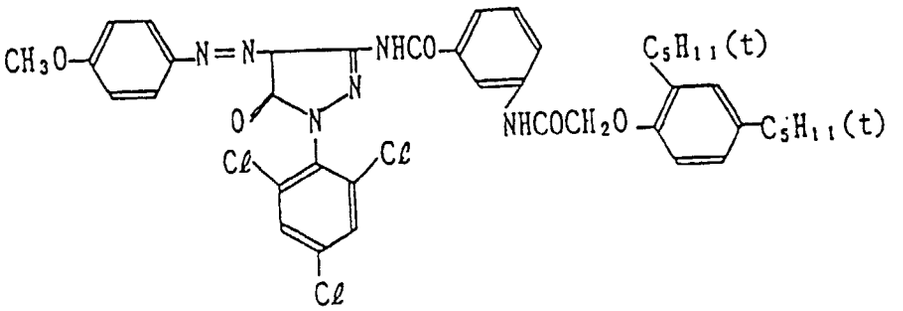
Y - 1



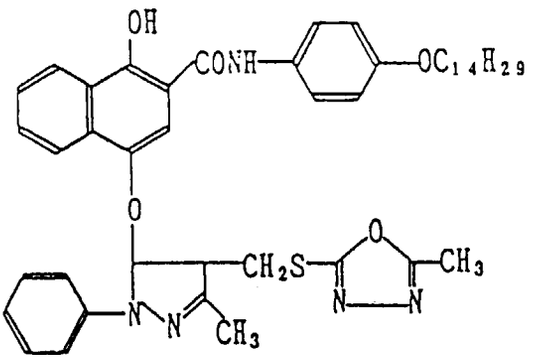
CC - 1



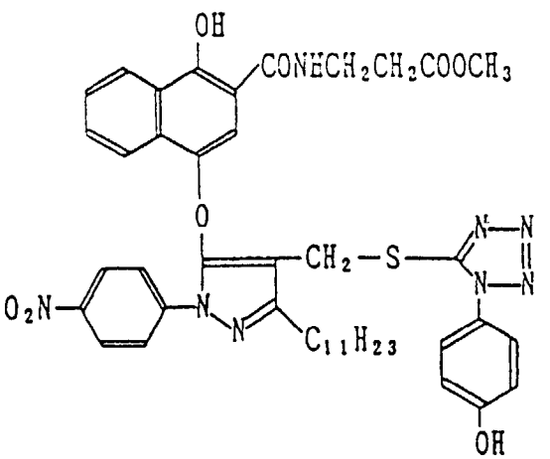
CM - 1



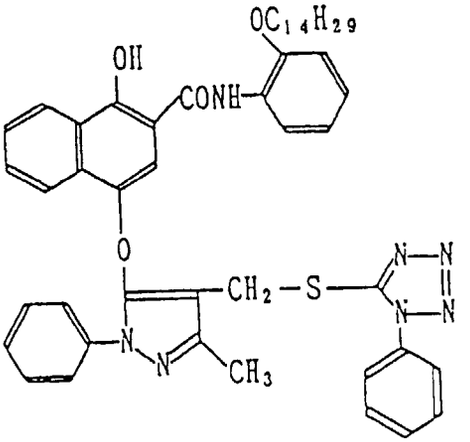
D - 1



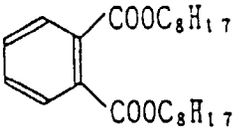
D - 2



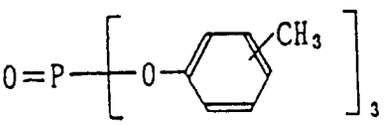
D - 3



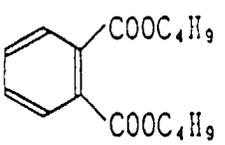
Oil - 1



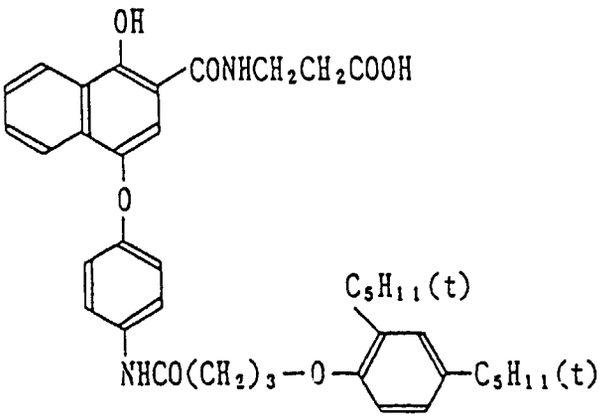
Oil - 2



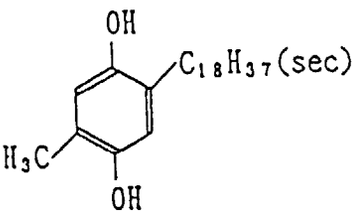
Oil - 3



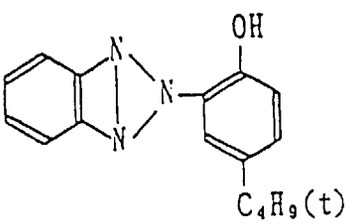
SC - 1



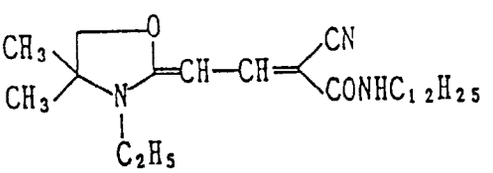
SC - 2



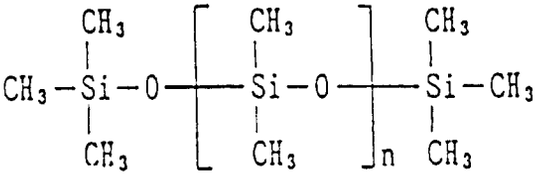
UV - 1



UV - 2

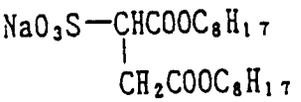


WAX - 1

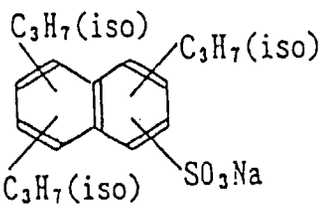


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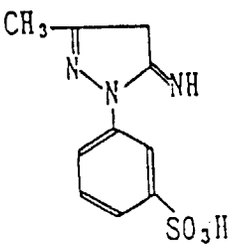
Su - 1



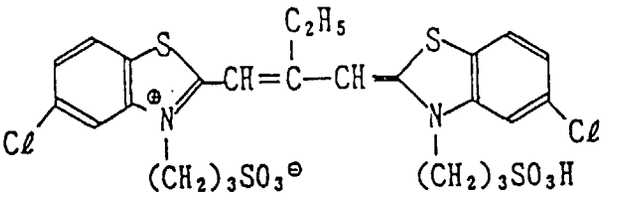
Su - 2



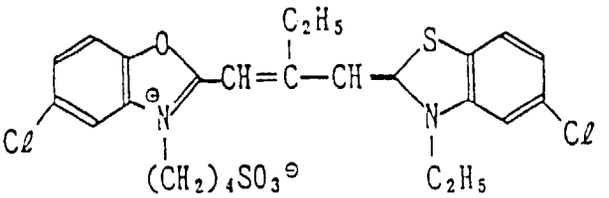
HS - 1



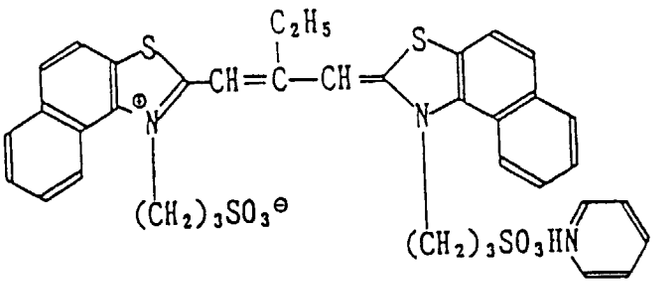
SD - 1



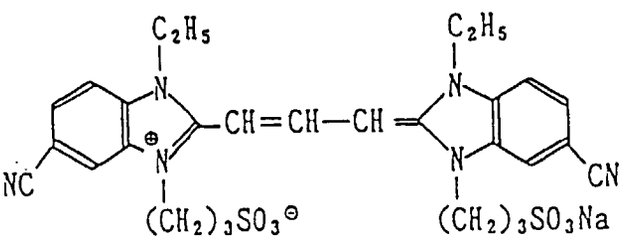
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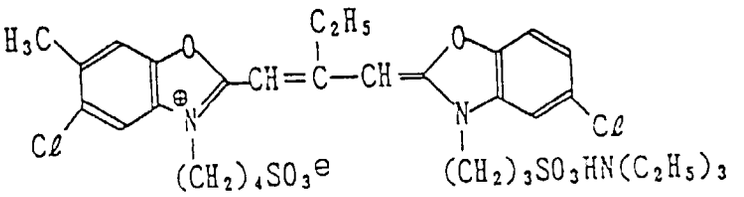
SD - 3



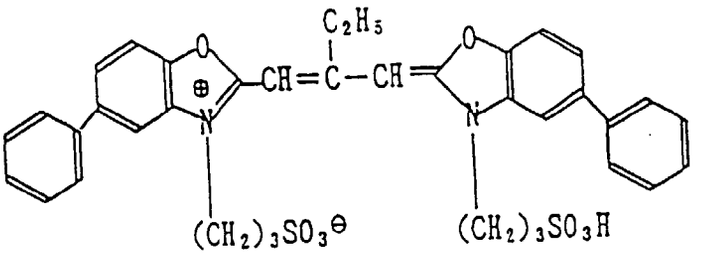
SD - 4



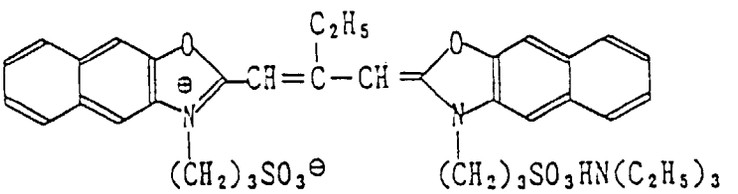
SD - 5



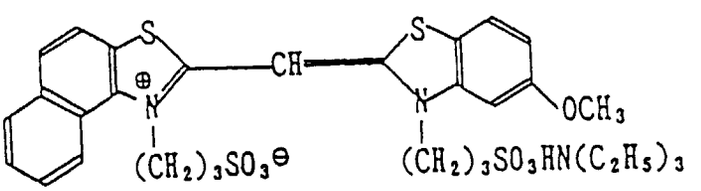
SD - 6



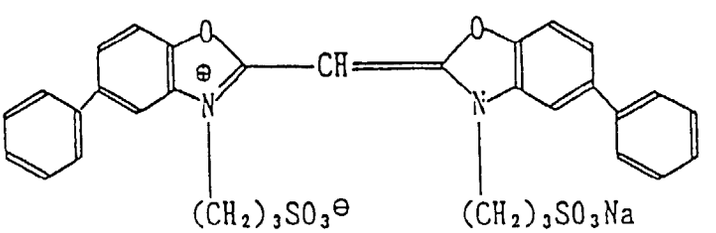
SD - 7



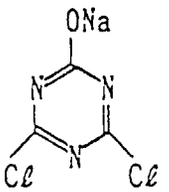
SD - 8



SD - 9



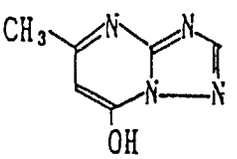
H - 1



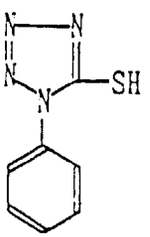
H - 2

$(CH_2=CHSO_2CH_2)_2O$

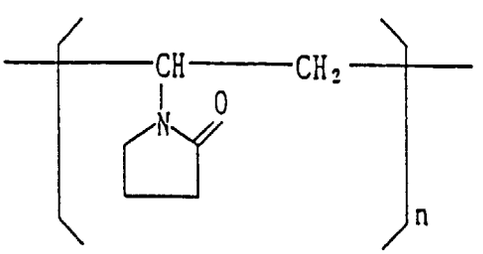
ST - 1



AF - 1

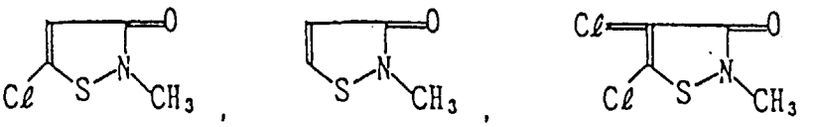


AF - 2



n : degree of polymerization

DI - 1 (Mixture of the following three components)



(Component A) (Component B) (Component C)

A : B : C = 50 : 46 : 4 (by molar ratio)

The samples thus prepared were given sensitometric exposure to white light and processed by the following scheme to evaluate sensitivity and RMS granularity.

Processing scheme (38°C)	Time
Color development	3 min and 15 sec
Bleaching	6 min and 30 sec
Washing with water	3 min and 15 sec
Fixing	6 min and 30 sec
Washing with water	3 min and 15 sec
Stabilizing	1 min and 30 sec
Drying	

The processing solutions used in this scheme had the following formulas.

Color developing solution

4-Amino-3-methyl-N-ethyl-N-(ß-hydroxyethyl)aniline sulfate	4.75 g
Anhydrous sodium sulfite	4.25 g
Hydroxylamine hemisulfate	2.0 g
Anhydrous potassium carbonate	37.5 g
Sodium bromide	1.3 g
Nitrilotriacetic acid trisodium salt (monohydrate)	2.5 g
Potassium hydroxide	1.0 g
Water	to make 1,000 ml
pH	adjusted to 10.0

Bleaching solution	
Ethylenediaminetetraacetic acid iron (III) ammonium salt	100 g
Ethylenediaminetetraacetic acid diammonium salt	10.0 g
Ammonium bromide	150.0 g
Glacial acetic acid	10.0 g
Water	to make 1,000 ml
pH	adjusted to 6.0 with aqueous ammonia

Fixing solution	
Ammonium thiosulfate	175.0 g
Anhydrous sodium sulfite	8.5 g
Sodium metasulfite	2.3 g
Water	to make 1,000 ml
pH	adjusted to 6.0 with acetic acid

Stabilizing solution	
Formaldehyde (37% aq. sol.)	1.5 ml
Konidax (Konica Corp.)	7.5 ml
Water	to make 1,000 ml

The "relative sensitivity (S)" is the relative value of the reciprocal of light reception that gives a fog density + 0.1, with the green sensitivity of sample 11 being taken as 100.

The "RMS" granularity is 1,000 times the standard deviation of the variation in density that occurs when a density equivalent to fog density + 1.0 is scanned with a microdensitometer having a scanning aperture area of 250 μm^2, with the RMS value of sample 11 being taken as 100.

Table 6 shows in relative values the results of evaluating the sensitivities and RMS granularities of coated samples 11 - 18 using Em-1 to Em-8, respectively.

Table 6

Sample No.	Emulsion No.	Relative sensitivity	RMS (in relative values)	Remarks
11	Em-1	100	100	Comparison
12	Em-2	95	107	do.
13	Em-3	101	116	do.
14	Em-4	98	107	do.
15	Em-5	115	84	Invention
16	Em-6	128	77	do.
17	Em-7	133	72	do.
18	Em-8	125	81	do.

As Table 6 shows, the samples (Nos. 15 - 18) that used silver halide photographic emulsions (Em-5 to Em-8) within the scope of the present invention exhibited better performance than the samples using the comparative emulsions in terms of both relative sensitivity and RMS granularity. Particularly good performance was exhibited by the samples (Nos. 16 and 17) that used Em-6 and Em-7, respectively.

Example 2

The same samples of multi-layered color photographic material as prepared in Example 1 were stored under the

following two different conditions and, thereafter, the samples were evaluated as in Example 1.
Condition A: stored at 65°C × 30 % r.h. for 4 days
Condition B: stored at 50°C × 80 % r.h. for 4 days

The results are shown in Table 7 below.

Table 7

Sample No.	Emulsion No.	Condition A		Condition B		Remarks
		Relative sensitivity	RMS	Relative sensitivity	RMS	
11	Em-1	100	100	100	100	Comparison
12	Em-2	90	115	93	120	do.
13	Em-3	88	121	90	126	do.
14	Em-4	92	113	90	118	do.
15	Em-5	114	83	115	84	Invention
16	Em-6	120	79	125	82	do.
17	Em-7	124	76	123	77	do.
18	Em-8	116	82	116	84	do.

As Table 7 shows, irrespective of whether the storage condition was A or B, the samples (Nos. 15 - 18) that used silver halide photographic emulsions (Em-5 to Em-8) within the scope of the present invention exhibited better performance than the samples using the comparative emulsions in terms of both relative sensitivity and RMS granularity. Particularly good performace was exhibited by the samples (Nos. 16 and 17) that used Em-6 and Em-7, respectively.

As is clear from the foregoing description, the present invention offers a silver halide photographic emulsion that yields silver halide photographic materials having high sensitivity, good graininess and satisfactory keeping quality.

Claims

1. A light-sensitive silver halide photographic emulsion comprising tabular silver halide grains, each of said tabular silver halide grains having an internal phase and an outermost layer that have different silver iodide contents characterized in that;
said tabular halide grains have a total projected area of at least 50% of all the grains in said emulsion the average silver iodide content of said tabular silver halide grains being at least 5 mol%, said internal phase having a silver iodide content of at least 18 mol %, said outermost layer having a silver iodide content of not more than 0.4 mol%, and in that a sectional plane cutting each of at least 50% in number of all the tabular silver halide grains in a direction that passes through the center of said tabular silver halide grain and being perpendicular to two parallel major faces satisfies the following relation:

$$90/100 \leq a/b \leq 100/90$$

where a is an average silver iodide content of a region defined by a distance over 9d/20 as measured from the center of said tabular silver halide grain in a direction perpendicular to the major faces, where d is the distance between the two parallel major faces in association with the sectional plane, and b is an average silver iodide content of a region defined by a distance over 91/20 as measured from the center of said tabular silver halide grain in a direction parallel to the major faces, where l is the distance between two opposing surfaces of the grain as measured in a direction that passes through the centre of said tabular silver halide grain and which is parallel to the major faces in association with the sectional plane.

2. A silver halide photographic emulsion according to claim 1 wherein said tabular silver halide grains have an average aspect ratio of from 1 to less than 5.

3. A silver halide photographic emulsion according to claim 1 wherein said tabular silver halide grains have a diameter

of 0.1 - 5.0 μm.

4. A silver halide photographic emulsion according to claim 1 wherein said tabular silver halide grains assume at least 60 % of the total projected area of all silver halide grains present.

5. A silver halide photographic emulsion according to claim 1 wherein said tabular silver halide grains are monodispersed.

6. A silver halide photographic emulsion according to claim 1 wherein at least 50 % in number of said tabular silver halide grains are comprised of the major faces in the shape of hexagon.

7. A silver halide photographic emulsion according to claim 1 wherein said tabular silver halide grains have an average silver iodide content of at least 5.5 mol%.

8. A silver halide photographic emulsion according to claim 1 wherein said internal phase has a silver iodide, content of at least 20 mol%.

9. A silver halide photographic emulsion according to claim 1 wherein said tabular silver halide grains have an average silver iodide content of no more than 0.3 mol% in the outermost layer.

10. A silver halide photographic emulsion according to claim 1 which satisfies the relation: $92/100 \leq a/b \leq 100/92$, where a and b have the same meanings as defined in claim 1.

11. A light-sensitive silver halide photographic emulsion comprising tabular silver halide grains, each of said tabular silver halide grains having an internal phase and an outermost layer that have different silver iodide contents, characterized in that said tabular silver halide grains have a total projected area of at leat 50% of all the grains in said emulsion, the average silver iodide content of said tabular silver halide grains is at least 5 mol%, said internal phase having a silver iodide content of at least 18 mol%, said outermost layer having a silver iodide content of not more than 0.4 mol%, and in that a sectional plane cutting substantially each of said tabular silver halide grains in a direction that passes through the center of said tabular silver halide grain and being perpendicular to two parallel major faces satisfies the relation:

$$90/100 \leq a/b \leq 100/90$$

as defined in claim 1.

Patentansprüche

1. Lichtempfindliche photographische Silberhalogenidemulsion, enthaltend tafelförmige Silberhalogenidkörner, wobei jedes der tafelförmigen Silberhalogenidkörner einen Kern und eine Schale mit unterschiedlichen Silberiodidgehalten aufweist, dadurch gekennzeichnet, daß
die tafelförmigen Silberhalogenidkörner eine Gesamtprojektionsfläche von mindestens 50% aller Körner in der Emulsion aufweisen, wobei der durchschnittliche Silberiodidgehalt der tafelförmigen Silberhalogenidkörner mindestens 5 Mol-% beträgt, der Kern einen Silberiodidgehalt von mindestens 18 Mol-% und die Schale einen Silberiodidgehalt von höchstens 0,4 Mol-% aufweist, und daß eine Schnittebene, die jedes von mindestens 50% der Anzahl aller tafelförmigen Silberhalogenidkörner in einer durch das Zentrum des tafelförmigen Silberhalogenidkorns hindurchgehenden Richtung schneidet und zu zwei parallelen Hauptflächen senkrecht liegt, der folgenden Beziehung genügt:

$$90/100 \leq a/b \leq 100/90,$$

worin a den durchschnittlichen Silberiodidgehalt eines Bereichs, der durch einen Abstand von über 9d/20 vom Zentrum des tafelförmigen Silberhalogenidkorns in einer zu den Hauptflächen senkrechten Richtung definiert ist, wobei d den Abstand zwischen den beiden mit der Schnittebene assoziierten parallelen Hauptflächen bedeutet, und b den durchschnittlichen Silberhalogenidgehalt eines Bereichs, der durch einen Abstand von über 91/20 vom

Zentrum des tafelförmigen Silberhalogenidkorns in einer zu den Hauptflächen parallelen Richtung definiert ist, wobei 1 den Abstand zwischen zwei einander gegenüberliegenden Flächen des Korns in einer durch das Zentrum des tafelförmigen Silberhalogenidkorns hindurchgehenden und zu den mit der Schnittfläche assoziierten Hauptflächen parallelen Richtung bedeutet, bedeutet.

2. Photographische Silberhalogenidemulsion nach Anspruch 1, wobei die tafelförmigen Silberhalogenidkörner ein durchschnittliches Aspektverhältnis von 1 bis unter 5 aufweisen.

3. Photographische Silberhalogenidemulsion nach Anspruch 1, wobei die tafelförmigen Silberhalogenidkörner einen Durchmesser von 0,1 - 5,0 µm aufweisen.

4. Photographische Silberhalogenidemulsion nach Anspruch 1, wobei die tafelförmigen Silberhalogenidkörner mindestens 60% der Gesamtprojektionsfläche aller vorhandenen Silberhalogenidkörner einnehmen.

5. Photographische Silberhalogenidemulsion nach Anspruch 1, wobei die tafelförmigen Silberhalogenidkörner monodispers sind.

6. Photographische Silberhalogenidemulsion nach Anspruch 1, wobei mindestens 50% der Anzahl der tafelförmigen Silberhalogenidkörner aus Hauptflächen in Form eines Hexagons bestehen.

7. Photographische Silberhalogenidemulsion nach Anspruch 1, wobei die tafelförmigen Silberhalogenidkörner einen durchschnittlichen Silberiodidgehalt von mindestens 5,5 Mol-% aufweisen.

8. Photographische Silberhalogenidemulsion nach Anspruch 1, wobei der Kern einen Silberiodidgehalt von mindestens 20 Mol-% aufweist.

9. Photographische Silberhalogenidemulsion nach Anspruch 1, wobei die tafelförmigen Silberhalogenidkörner in der Schale einen durchschnittlichen Silberiodidgehalt von höchstens 0,3 Mol-% aufweisen.

10. Photographische Silberhalogenidemulsion nach Anspruch 1, die der folgenden Beziehung genügt: $92/100 \leq a/b \leq 100/92$, worin a und b die in Anspruch 1 angegebene Bedeutung haben.

11. Lichtempfindliche photographische Silberhalogenidemulsion, enthaltend tafelförmige Silberhalogenidkörner, wobei jedes der tafelförmigen Silberhalogenidkörner einen Kern und eine Schale mit unterschiedlichen Silberiodidgehalten aufweist, dadurch gekennzeichnet, daß die tafelförmigen Silberhalogenidkörner eine Gesamtprojektionsfläche von mindestens 50% aller Körner in der Emulsion aufweisen, wobei der durchschnittliche Silberiodidgehalt der tafelförmigen Silberhalogenidkörner mindestens 5 Mol-% beträgt, der Kern einen Silberiodidgehalt von mindestens 18 Mol-% und die Schale einen Silberiodidgehalt von höchstens 0,4 Mol-% aufweist, und daß eine Schnittebene, die im wesentlichen jedes der tafelförmigen Silberhalogenidkörner in einer durch das Zentrum des tafelförmigen Silberhalogenidkorns hindurchgehenden Richtung schneidet und zu zwei parallelen Hauptflächen senkrecht liegt, der folgenden Beziehung genügt:

$$90/100 \leq a/b \leq 100/90,$$

die wie in Anspruch 1 definiert ist.

Revendications

1. Emulsion photographique à halogénure d'argent photosensible comprenant das grains d'halogénure d'argent tabulaires, chacun desdits grains d'halogénure d'argent tabulaires ayant une phase interne et une couche la plus externe qui ont des teneurs en iodure d'argent différentes, caractérisée en ce que;
lesdits grains d'halogénure tabulaires ont une surface totale de projection d'au moins 50% de la totalité des grains dans ladite émulsion, la teneur en iodure d'argent moyenne desdits grains d'halogénure d'argent tabulaires étant d'au moins 5% en moles, ladite phase interne ayant une teneur en iodure d'argent d'au moins 18% en moles, ladite couche la plus externe ayant une teneur en iodure d'argent de pas plus de 0,4% en moles, et en ce qu'un plan sectionnel coupant chacun d'au moins 50% en nombre de la totalité des grains d'halogénure d'argent tabu-

laires dans une direction qui passe à travers le centre dudit grain d'halogénure d'argent tabulaire et étant perpendiculaire à deux faces principales parallèles satisfait la relation suivante:

$$90/100 \leq a/b \leq 100/90$$

où a est une teneur en iodure d'argent moyenne d'une région définie par une distance sur 9d/20 comme mesurée à partir du centre dudit grain d'halogénure d'argent tabulaire dans une direction perpendiculaire aux deux faces principales, où d est la distance entre les deux faces principales parallèles en association avec le plan sectionnel, et b est une teneur en iodure d'argent moyenne d'une région définie par une distance sur 91/20 comme mesurée à partir du centre dudit grain d'halogénure d'argent tabulaire dans une direction parallèle aux faces principales, où 1 est la distance entre deux faces opposées du grain comme mesurée dans une direction qui passe à travers le centre dudit grain d'halogénure d'argent tabulaire et qui est parallèle aux faces principales en association avec le plan sectionnel.

2. Emulsion photographique à halogénure d'argent selon la revendication 1, dans laquelle lesdits grains d'halogénure d'argent tabulaires ont un rapport d'aspect moyen de 1 à moins de 5.

3. Emulsion photographique à halogénure d'argent selon la revendication 1, dans laquelle lesdits grains d'halogénure d'argent tabulaires ont un diamètre de 0,1-5,0 μm.

4. Emulsion photographique à halogénure d'argent selon la revendication 1, dans laquelle lesdits grains d'halogénure d'argent tabulaires couvrent au.moins 60% de la surface totale de projection de la totalité des grains d'halogénure d'argent présents.

5. Emulsion photographique à halogénure d'argent selon la revendication 1, dans laquelle lesdits grains d'halogénure d'argent tabulaires sont monodispersés.

6. Emulsion photographique à halogénure d'argent selon la revendication 1, dans laquelle au moins 50% en nombre desdits grains d'halogénure d'argent tabulaires sont constitués des faces principales en forme d'hexagone.

7. Emulsion photographique à halogénure d'argent selon la revendication 1, dans laquelle lesdits grains d'halogénure d'argent tabulaires ont une teneur en iodure d'argent moyenne d'au moins 5,5% en moles.

8. Emulsion photographique à halogénure d'argent selon la revendication 1, dans laquelle ladite phase interne a une teneur en iodure d'argent d'au moins 20% en moles.

9. Emulsion photographique à halogénure d'argent selon la revendication 1, dans laquelle lesdits grains d'halogénure d'argent tabulaires ont une teneur en iodure d'argent moyenne de pas plus de 0,3% en moles dans la couche la plus externe.

10. Emulsion photographique à halogénure d'argent selon la revendication 1, qui satisfait la relation $92/100 \leq a/b \leq 100/92$, où a et b ont les mêmes significations comme définies à la revendication 1.

11. Emulsion photographique à halogénure d'argent photosensible comprenant des grains d'halogénure d'argent tabulaires, chacun desdits grains d'halogénure d'argent tabulaires ayant une phase interne et une couche la plus externe qui ont des teneurs en iodure d'argent différentes, caractérisée en ce que lesdits grains d'halogénure d'argent tabulaires ont une surface totale de projection d'au moins 50% de la totalité des grains dans ladite émulsion, la teneur en iodure d'argent moyenne desdits grains d'halogénure d'argent tabulaires est d'au moins 5% en moles, ladite phase interne ayant une teneur en iodure d'argent d'au moins 18% en moles, ladite couche la plus externe ayant une teneur en iodure d'argent de pas plus de 0,4% en moles, et en ce qu'un plan sectionnel coupant essentiellement chacun desdits grains d'halogénure d'argent tabulaires dans une direction qui passe à travers le centre dudit grain d'halogénure d'argent tabulaire et étant perpendiculaire à deux faces principales parallèles satisfait la relation:

$$90/100 \leq a/b \leq 100/90$$

comme définie à la revendication 1.